# A comparison of pilot scale electron beam and bench scale gamma irradiations of cyanide aqueous in solution

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**Abstract** Bench-scale gamma irradiation was conducted to investigate the influencing factors, such as initial cyanide concentration, absorbed dose, saturated gases, and pH value as well as water compositions on the γ radiolysis of cyanide in simulated aqueous solution. The decomposition rate of cyanide was observed as pseudo-first-order kinetic over the applied concentrations varied from 77 mg/L to 247 mg/L. Cyanide was decomposed more rapidly at a lower initial concentration than that at a higher initial concentration. However, the radical scavengers in natural waters, such as carbonate and bicarbonate, have negative effects on the remove of cyanide. This indicated that hydroxyl radical may play predominant role in the γ radiolysis of aqueous cyanide. Finally, ammonia and cyanate were identified as the main nitrogen-containing byproduct of γ radiolysis of cyanide. To remove toxic hydrogen cyanide (HCN) from carbon fiber industry waste gases, a pilot-scale experiment with a self-sheltered electron beam accelerator was demonstrated after two sprays of chemical absorption. The operating conditions for absorption and irradiation had been optimized. It was shown that after the first spray tower, HCN concentration decreased from $(240\pm50)$ mg/m$^3$ to $35 \pm 15$ mg/m$^3$. While after the second spray tower, effluent HCN was reduced almost below the method detection limit. Then, the residual cyanide in aqueous solution was exposed to high energy electron beam (EB). Influent CN$^-$ concentration was controled at $(15\pm2)$ mg/L with a water regulating tank. This treatment allows CN$^-$ to reach the regional limit (of 0.5 mg/L) for safe industrial wastewater discharge with a irradiation dose of 12 kGy. The obtained results showed that the combined process were effective for removing HCN from the waste gas.

**Key words** Gamma irradiation, Electron beam, Wastewater treatment, Cyanide, Ozone, Advanced oxidation processes

## 1   Introduction

HCN and other cyano-compounds that liberate free cyanide ions (CN$^-$) are highly toxic to almost all forms of fauna[1]. They are bound with cytochrome oxidase to inhibit its activity and induce cellular anoxia. It is relatively easy to obtain cyanide, because it is being widely used in metal cleaning, electroplating, steel tempering, ore leaching, metal processing and other chemical industries[2]. Therefore, control and remediation of cyanide contaminated gas and water is usually desired. Typical technical methods include biodegradation, alkaline chlorination, hydrogen peroxide and ozonation, etc. But all these processes have several disadvantages. Biological oxidation may require long adaptation and can not treat high concentrations[3]. Chlorine can react with organics to form chlorinated compounds[4] and may result in huge amount of total dissolved solids (TDS) in the treated water[5]. Hydrogen peroxide is successful in oxidizing cyanides only in the presence of copper as catalyst, which have to be separated and then recycled from the purified wastewater subsequently[6]. Ozone makes the process burden with high reagent costs[7,8]. The SO$_2$/air

process is relatively inexpensive, but some of reagent savings are offset by license/royalty payments[9]. As a result, the development of a more cost-effective and environmentally friendly treatment process is desired.

Positive effects of ionizing radiation processing for environment protection are well known. Current status of the application includes radiation treatment of wastewater, sewage sludge, flue gases, solid wastes, etc.[10–13]. The principles of radiation treatment of wastewater may be explained by reaction (1)[14]. In reaction 1, hydroxyl radicals ($\cdot$OH, $E_0$=2.8V) is the strongest oxidation radical while hydrated electron ($e_{aq}^-$, $E_0$=–2.8V) and hydrogen atom ($\cdot$H, $E_0$=–2.1V) are main reducing species in water radiolysis. In most radiolysis solutions, the reactive primary species ($e_{aq}^-$, $\cdot$H and $\cdot$OH) may initial the decompositions of water pollutants.

$$H_2O \rightarrow 2.7\, e_{aq}^- + 0.6H + 2.8OH + 0.45H_2 + 0.7H_2O_2 + 2.7H^+ \qquad (1)$$
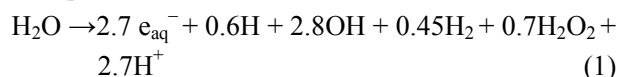
The objective of bench-scale $^{60}$Co γ-source experiments was to investigate gamma irradiation induced degradation kinetics of cyanide at different initial concentrations. Various influencing factors that are important to the decomposition of cyanide were studied, including absorbed dose, initial cyanide concentration, saturated gases, and initial solution pH and water compositions. Moreover, the principal reaction byproducts of γ radiolysis of cyanide, such as ammonia and cyanate, were quantitatively examined. Pilot-scale electron beam irradiation was demonstrated to explore the feasibility of the combined technology to eliminate the release of toxic cyanide containing gas produced from Zhong Fu Shen Ying Carbon Fiber Ltd., Jiangsu province, China. The obtained results of the study not only suggest that it is feasible to treat cyanide waste gas combined chemical absorbtion and radiation degradation, but also show a good demonstration for the application of ionizing radiation processing in the environmental protection in China.

## 2　Experimental

### 2.1　Irradiation experiments

Bench-scale experiments were performed upon a gamma irradiator, located at Institute of Nuclear and New Energy Technology (INET), Tsinghua University.

The $^{60}$Co-γ-source holder consists of 16 source rods, with a total activity of about $4.8\times10^{14}$ Bq. In our irradiation experiments, each time 25 mL of cyanide solution was first transferred to 50 mL Pyrex glass bottles and then placed in the $^{60}$Co irradiated field with a specific distance and time to achieve absorbed doses range from 5 to 35 kGy. Absorbed dose rate used in this study was fixed at 279 Gy/min, determined by means of a Fricke dosimeter using G ($Fe^{3+}$) =15.6[15].

Pilot plant irradiation were operated with a self-sheltered electron beam accelerator (EA, energy 0.5–1.0 MeV, beam current 10–15 mA), which was manufactured by Jiangsu Dasheng Electron Accelerator Device Co., Ltd. Aqueous streams of wastewater containing cyanide were exposed to a scanned beam in a waterfilm from two nozzles. The size of each nozzle is designed to 10 cm wide and 0.2 cm thick according to the penetration depth of radiation in water[16]. The average speed of the waterfilm through the beam is approximately 1.37 m/s. This yields a retention time of approximately 0.05 s and a flow about 1.82 m$^3$/h. The irradiation dose was calculated with a empirical formula described by Luo and Xu[17]. All experiments were carried out at ambient temperature.

### 2.2　Materials

KCN and other reagents were obtained from Beijing Chemical Co. Inc., China. All chemicals were of analytical grade or the highest purity available from the supplier. The sample solutions of cyanide were prepared in doubly distilled water or in the tap water of INET as the control. Operators were provided with personal musk and portable HCN gas monitor/alarm units. In order to investigate the effects of different saturated gases in radiolysis, nitrogen and oxygen gas was continuous bubbling into the aqueous solution during irradiation at the flow rate of 0.5 L/min, respectively. The purity of nitrogen and oxygen gases is more than 99.99 %.

### 2.3　Analytical methods

The concentration of CN$^-$ was determined by titration with silver nitrate standard solution[18] and iso-nicotinic acid and 1-phenyl-3-methyl-5-pyrazolone photometric method[19]. The changes of solution pH

during irradiation process were recorded by a WTW pH meter. Ammonia (measured as $NH_4^+$ ions) appeared to be one of the degradation products. Its yield was determined by means of Nessler's reagent measuring the absorption at $\lambda$=420 nm. Another byproduct of cyanate was converted to ammonia by acid hydrolyzing (Kjeldahl digestion), and then determined total ammonia by using Nessler's reagent, too. The difference of ammonia concentration before and after acid hydrolysis is the content of cyanate[20]. The pH of wastewater was adjusted using sulfuric acid and sodium hydroxide.

## 2.4 Pilot plant technical process

The technical process was showed in Fig.1. After the preliminary gas purification, the cyanide gas was passed through two spray towers in turn to make the treated gas in comply with national discharge standards (1.9 mg/m³). HCN was entrapped in absorption solution containing sodium hypochlorite. Then, the residual cyanide in aqueous solution was introduced into a process vessel and irradiated by a process of electron beams/ozonation.
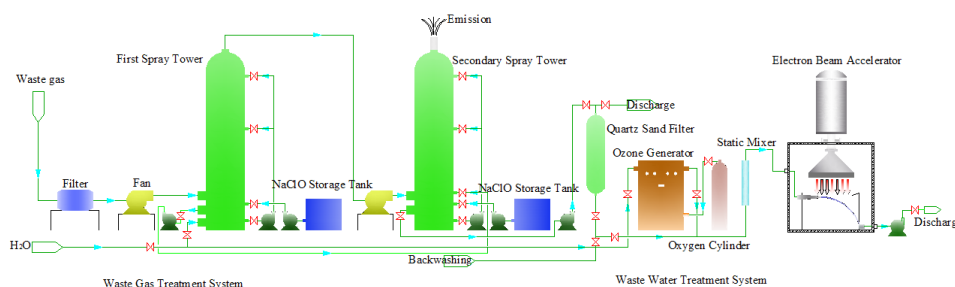


**Fig.1**   Schematic diagram of pilot plant technical process.

# 3    Results and discussion

## 3.1    Bench-scale experiments

### 3.1.1    Effects of initial concentrations

A series of batch experiments was conducted to evaluate the effect of initial concentrations on the cyanide decomposition by gamma irradiation. Initial concentrations of $CN^-$ were 85.9 mg/L, 131 mg/L and 247 mg/L, respectively. The initial solution pH before irradiation was 9.50. Fig.2 shows the removal of cyanide at different initial concentrations.
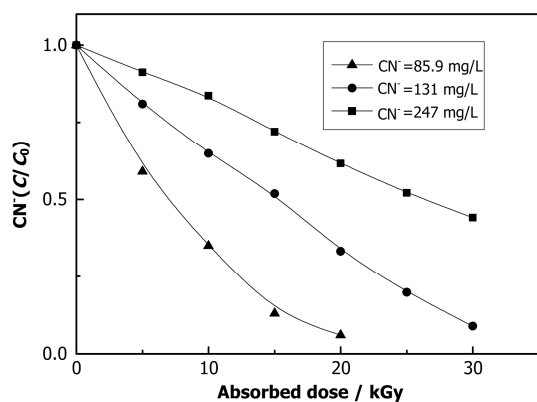


**Fig.2**    Removal of $CN^-$ at different initial concentration as a function of absorbed dose.

As would be seen, the rate of $CN^-$ degradation dramatically increased with the increasing absorbed dose. At the absorbed dose of 20 kGy, the removal rate were 83.8%, 66.8% and 38.4% at initial concentrations of 85.9 mg/L, 131 mg/L, 247 mg/L, respectively. The observation indicated that cyanide was removed more rapidly at a lower initial concentration than that at a higher initial $CN^-$ concentration. Similar results are reported in the literature for aromatic hydrocarbons[21] and dimethyl phthalate[22] degradation.

As previous studies using electron beam or gamma irradiation, the concentration of a pollutant decrease exponentially with absorbed dose, which can be expressed as the first-order model[23].

$$C = C_0 e^{-kD} \tag{2}$$

where $C_0$ and $C$ is the concentration of the pollutant before and after irradiation, respectively, $k$ is the dose constant in units of a reciprocal dose, and $D$ is the absorbed dose necessary to achieve the concentration change specified. For convenience, Eq.(2) was modified into Eq.(3), to compare the pollutant decomposition rates at the various conditions.
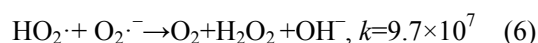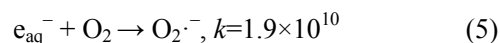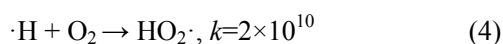
$$\ln\left[\frac{c}{c_0}\right] = kD \qquad (3)$$

Figure 3 shows the dependence of $\ln(C/C_0)$ on the function of increasing absorbed dose. The rate constants were calculated as $1.33 \times 10^{-4}$ Gy$^{-1}$, $5.66 \times 10^{-5}$ Gy$^{-1}$, and $2.54 \times 10^{-5}$ Gy$^{-1}$ at concentrations of 85.9 mg/L, 131 mg/L, 247 mg/L, respectively. As a conclusion, the dose constant is dependent on the initial concentration of CN$^-$ and decreases obviously as the concentration increases. This relationship is in agreement with the study on the radiolysis of polychlorinated biphenyls in nonpolar solution[24].
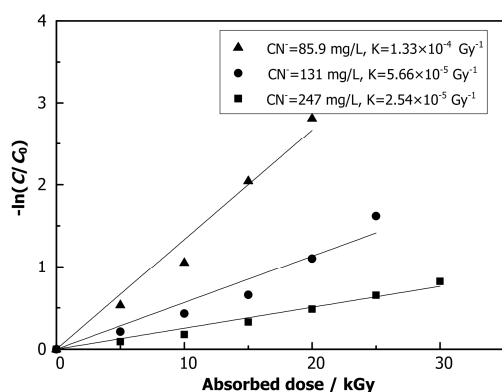


**Fig.3** Initial concentration dependency of the radiolytic decomposition rate constant.

### 3.1.2 Effects of saturated gases

Irradiation experiments were performed at static (situation A), N$_2$ (situation B) as well as O$_2$ (situation C) continuous bubbling conditions, respectively. The initial concentration of cyanide was 85.89 mg/L and the initial solution pH was adjusted to 10.08. In the presence of air or in water saturated with pure oxygen, $e_{aq}^-$ and ·H can react with oxygen as Reactions (4)–(6)[25]. Both $e_{aq}^-$ and ·H, at low pollutant concentration in aerated water, are converted into peroxyl-radicals. Depending on the O$_2$ as well as the cyanide concentration in the aqueous solution, a competition for $e_{aq}^-$ and ·H between O$_2$ and CN$^-$ takes place. Hence, the attacking species under these conditions are ·OH as well as O$_2$·$^-$/HO$_2$· which are leading to the corresponding cyanide-adducts.

$$\cdot H + O_2 \rightarrow HO_2\cdot,\ k = 2 \times 10^{10} \qquad (4)$$

$$e_{aq}^- + O_2 \rightarrow O_2\cdot^-,\ k = 1.9 \times 10^{10} \qquad (5)$$

$$HO_2\cdot + O_2\cdot^- \rightarrow O_2 + H_2O_2 + OH^-,\ k = 9.7 \times 10^7 \qquad (6)$$

According to the mechanism of radiolytic reactions involving pollutants, the radiation induced decomposition of varies pollutants from water and wastewater can be subdivided into four groups[26]. The effects of different saturated gases on the γ radiolysis of cyanide are shown in Fig.4.
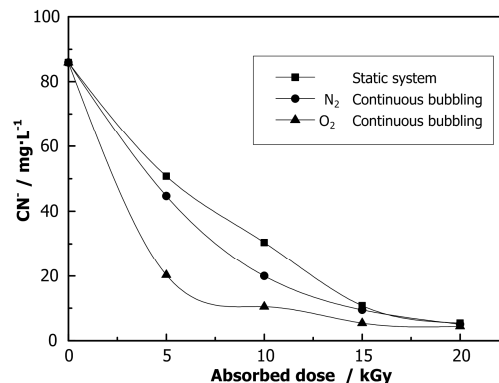


**Fig.4** Effects of aerated gases on γ radiolysis of cyanide solution.

At the dose of 5 kGy, CN$^-$ removal efficiency is 40.96%, 47.97%, 76.39% under the situation A, B, C, respectively. A possible explanation for such results is that ·OH radicals maybe the main attacking species meanwhile $e_{aq}^-$ and ·H directly attack to cyanide play a minor role. At situation B, excessive saturation N$_2$ causes the O$_2$ concentration in the solution down to almost zero. However, the CN$^-$ removal efficiency is better at situation B that than at situation A. A possible reason for this interesting phenomenon may duo to the decreasing of solution pH and N$_2$ stripping. As shown in Fig.5, the solution pH decreases slowly from 10.08 to 9.30 with the increasing absorbed dose.
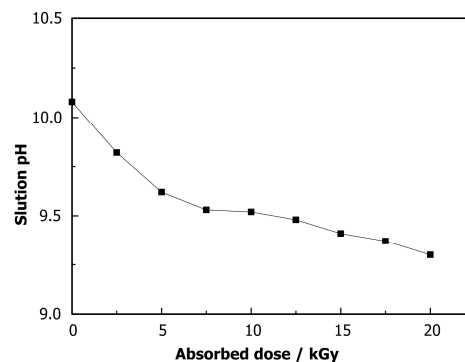


**Fig.5** Change of solution pH during irradiation process.

This situation is more conducive to the formation of HCN, which then stripped off by the bubbling of N$_2$. Similar results are reported for the removal of cyanide in gold leach waste solution by air

stripping[27]. It is also interesting to note that gamma irradiation can only reduce the $CN^-$ concentration to a certain extent. So, when the radiation dose increases from 10 kGy to 20 kGy, $CN^-$ concentration almost does not change while bubbling $O_2$, but slowly decreases under the other two conditions, and the removal efficiency of $CN^-$ was almost the same among the above three conditions at 20 kGy.

### 3.1.3 Effects of the initial solution pH

Figure 6 shows the dependency of the initial solution pH on the decomposition of $CN^-$. The initial $CN^-$ concentration was 85.89 mg/L. The pH before irradiation was adjusted to 9.97 and 11.7, respectively. The fact that the removal of $CN^-$ is less efficient at higher pH than that at lower pH was possible caused by the reducing or increasing active particles. The observation is similar to a previous study about decomposition of 2,4,6-trinitrotoluene by gamma irradiation[28]. Considering the above discussion that ·OH radicals maybe the main attacking species, a possible reason for the effects of the initial solution pH on degradation efficiency is the acid-alkali properties of ·OH radicals. Initial yields ($G_i$-value) of different reaction species produced by water radiolysis are variants to the change of solution pH. Such as $G_i$-value of $e_{aq}^-$ decreases, ·H increases rapidly, and ·OH increases slightly as the pH decreases below 5. Additionally, the $G_i$-value of ·OH and ·H decrease significantly while $O·^-$ and $e_{aq}^-$ increase rapidly as the pH increases above 10[16].
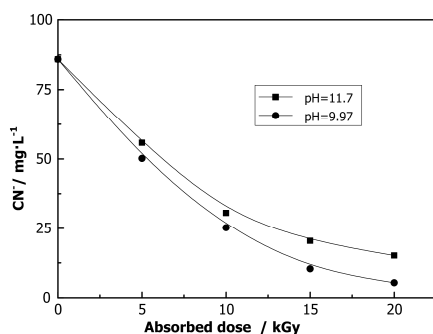


**Fig.6** Dependency of initial pH on γ radiolysis of cyanide solution.

### 3.1.4 Effect of water composition

The effect of water composition on the decomposition of cyanide was investigated by using distilled water and tap water with initial $CN^-$ concentration at 76.24 mg/L. Fig.7 shows that the decomposition of cyanide

almost reaches up to 100 % in the distilled water sample at a dose of 20 kGy. However, the removal rate decreases to 69.5% in the tap water sample at the same absorbed dose. The observation indicates that the cyanide degradation is effected by the presence of some ions in the tap water. These ions, such as carbonate/bicarbonate ions, may interact with the reactive species formed during irradiation as reactions shown below[29].

$$CO_3^{2-} + ·OH \rightarrow CO_3·^- + OH^-, k=3.9×10^8 \quad (7)$$
$$HCO_3^- + ·OH \rightarrow CO_3·^- + H_2O, k=8.5×10^6 \quad (8)$$
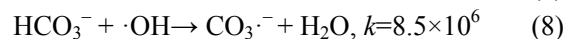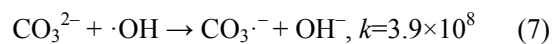
It had been demonstrated earlier that the decomposition of trichloroethylene (TCE) and perchloroethylene (PCE) was significantly inhibited by these ions in the natural or drinking water. According to Yoon *et al.*[30], without carbonate ions, TCE and PCE decomposition were abruptly increased at a dose of 100 Gy and reached up to 100% at 300 Gy. However, only around 20% of PCE was removed in the presence of $5×10^{-3}$ mol/L carbonate ions while just 5 % of TCE was removed under the same condition.
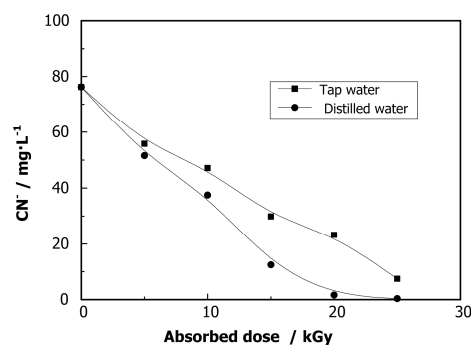


**Fig.7** Effects of water composition on γ–radiolysis of cyanide solution.

### 3.1.5 Analysis of degradation products

To study the intermediate products of γ radiolysis of cyanide solution, experiments were carried out in static system at pH 9.97 and an initial $CN^-$ concentration of 85.89 mg/L. Ammonia ($NH_4^+$) and cyanate ($CNO^-$) were detected as the main byproducts instead of nitrogen gas.

Fig.8 shows the concentrations of residual $CN^-$, $CNO^-$ and $NH_4^+$ as a function of the absorbed dose. At the beginning of irradiation, the concentration of $CNO^-$ increased sharply, and reached the highest value at the dose of 5 kGy. However, with the increasing absorbed dose from 5 kGy to 20 kGy, $CNO^-$
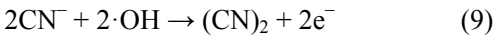
concentration decreased slowly might due to the hydrolysis reactions in alkaline solution[31]. Whereas the concentration of $NH_4^+$ increased slowly during the whole irradiation process and reached 32.24 mg/L at 20 kGy. In fact, even at 20 kGy, transformation rate from $CN^-$ to $NH_4^+$ was only 57.3 % (Fig.8).
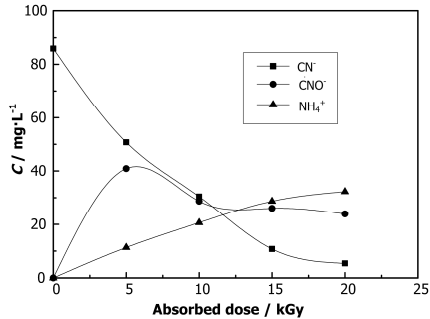


**Fig.8** $CN^-$, $CNO^-$ and $NH_4^+$ concentration profile during γ-irradiation.
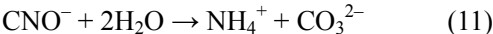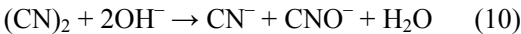
The observation indicated that $CN^-$ might be first reaction with ·OH to form $(CN)_2$, which then converted to $CN^-$ and $CNO^-$ in alkaline solution, and the latter then hydrolyzed to $NH_4^+$ and $CO_3^{2-}$. Another degradation manner might be the direct oxidation by $H_2O_2$ and ·$HO_2$, as Reactions (12) and (13) which were similar to previous studies[32,33].

$$2CN^- + 2·OH \rightarrow (CN)_2 + 2e^- \qquad (9)$$

$$(CN)_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \qquad (10)$$

$$CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-} \qquad (11)$$

$$CN^- + 2HO_2 + 2OH^- \rightarrow CNO^- + 2HO_2^- + H_2O \qquad (12)$$

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O \qquad (13)$$

However, if carbonate or bicarbonate anions were verified as the main carbon-containing byproduct of γ radiolysis of cyanide, according to the dicussion in 3.1.4, it can be deduced that the increased carbonate or bicarbonate concentration with the increasing initial cyanide concentration and absorbed dose, which, in turn, inhibits cyanide radiolysis due to the scavengers of hydroxyl radical.

### 3.2 Pilot plant experiments

#### 3.2.1 Waste gas treatment system

The main ingredients of the waste gas produced in the carbonization process were HCN, CO, $NH_3$, $CH_4$, silicone oil, etc. The velocity of waste gas was 5–6 m/s and the flow was 8000–10000 m³/h. The dosing quantity of sodium hypochlorite was 220 kg/h and 80 kg/h for the first and second spray tower, respectively. The pH value of the first and second spray tower was 11, 9, respectively. Some results of our study are given in Table 1.

**Table 1** Concentration of HCN, $NH_3$ at different sampling points

| HCN concentration (mg/m³) | | | $NH_3$ concentration (mg/m³) | | |
|---|---|---|---|---|---|
| Inlet | Exit of the first spray tower | Exit of the second spray tower | Inlet | Exit of the first spray tower | Exit of the second spray tower |
| 208.13 | 22.54 | 0.82 | 24.99 | 135.26 | 146.58 |
| 242.14 | 27.57 | 1.33 | 34.09 | 158.25 | 161.24 |
| 263.08 | 40.49 | 1.89 | 52.21 | 189.15 | 206.73 |
| 288.69 | 49.16 | 1.83 | 57.18 | 204.28 | 221.08 |

Vaidya *et al.*[34] had validated that it was an appropriate treatment process for disposal of cyanide by alkali chlorination with calcium hypochlorite. The table shows that it is also effective for cyanide removal by sodium hypochlorite with sodium hydroxide. The removal efficiency of cyanide gas with two spray towers was almost about 100%. After the first spray tower, HCN concentration decreased from about (240±50) mg/m³ to (35±15) mg/m³. While after the second spray tower, effluent HCN concentration was reduced almost below the method detection limit. At the same time, $NH_3$ concentration increased from (41±16) mg/m³ to (170±35) mg/m³ after the first stage of absorption, and to (183±37) mg/m³ after the second

stage of absorption. That is to say, ammonia is one of the detected endproduct of cyanide. Similar results are reported by Kao *et al.*[35], who have shown that klebsiella oxytoca is able to biodegrade cyanide to non-toxic endproducts such as ammonia.

#### 3.2.2 Wastewater treatment system

**Effects of initial concentrations:** Pilot experiments were carried out to study the variations of different initial cyanide concentration at pH 9.8. The changes of cyanide concentration as a function of irradiation dose are presented in Figs.(9) and (10).

It is interesting to note that the degradation trend is consistent with the bench scale experiments. As it is seen from Fig.9, cyanide was removed more

rapidly at a lower initial CN⁻ concentration than that at a higher initial concentration. At an irradiation dose of 1.5 kGy, the removal efficiency were 59.25%, 42.17% and 33.88%, corresponding to the initial CN⁻ concentration at 21.08 mg/L, 55.63 mg/L and 117.49 mg/L. Mudliar *et al.*[36] reported that advanced oxidation processes such as ultra violet light, hydrogen peroxide and ozone were feasibile options for treatment and disposal of cyanide containing industrial wastewater. From Figs.(9) and (10), it can be seen that electron beam irradiation is also a feasible way to achieve complete removal of cyanide from wastewater at an acceptable irradiation dose. When the initial CN⁻ concentration were 21.08 mg/L and 55.63 mg/L, an irradiation dose of 6 kGy and 9 kGy were required respectively to make the treated wastewater in comply with national discharge standards. While with higher initial CN⁻ concentration such as 117.49 mg/L and 212.89 mg/L, a higher irradiation dose of 15 kGy and 27 kGy were needed.

**Effects of the initial solution pH:** To study the effects of the initial pH on electron beam radiolysis of cyanide solution, experiments were performed with initial CN⁻ concentration at 55.63 mg/L. The pH of wastewater was adjusted to 8.51, 9.88 and 12.07. Results are presented in Fig.11.

From Fig.11, it can be seen that CN⁻ concentration decreased with increasing irradiation dose, but cyanide degradation efficiency was almost the same at pH 8.51 and 9.88. For example at an irradiation dose of 1.5 kGy, CN⁻ removal efficiency was 40.39% and 42.17%, respectively. However, it was only 29.59% at pH 12.07. At irradiation dose of 10.5 kGy, CN⁻ concentration decreased to 0.67 mg/L, 0.86 mg/L and 2.13 mg/L, corresponding to the pH 8.51, 9.88 and 12.07. The former two concentrations had reached national emission standards. However, the third concentration exceeded the standards of 113%. Since ·OH radicals maybe the main attacking species as discussed above, a possible cause for such results would be attributable to an decrease in the ·OH radical as pH>11.

**Effects of O₃, EB and EB+O₃:** It is generally thought that O₃ can increase the effectiveness of ionizing irradiation due to the fact that it leads to an increase in oxidizing species concentration[25,37], as

reactions showed (14)–(18). The synergetic effect with O₃ on the radiolysis decomposition of refractory compounds has been reported before[38,39]. To investigate the effect of O₃ on cyanide degradation, a series of experiments were performed at an irradiation dose of 1.5 kGy, at pH 9.56, at O₃ concentration of 2 mg/L. Results are shown in Fig.12.
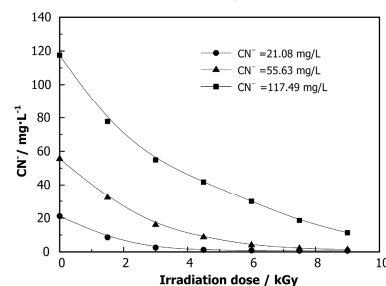


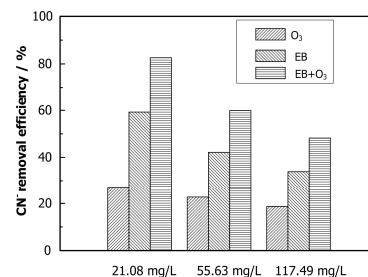**Fig.9** Effects of initial concentrations on electron beam radiolysis of cyanide solution.
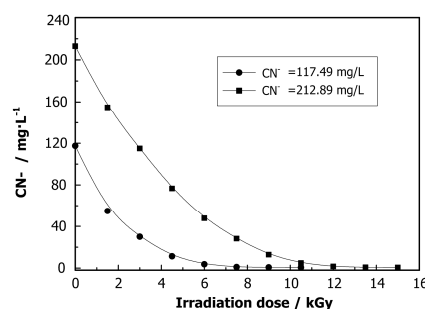


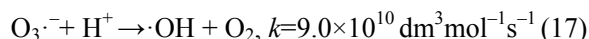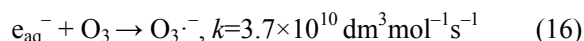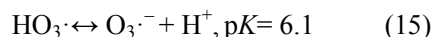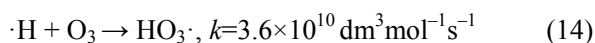**Fig.10** Decrease of higher initial CN⁻ concentration as a function of irradiation dose.
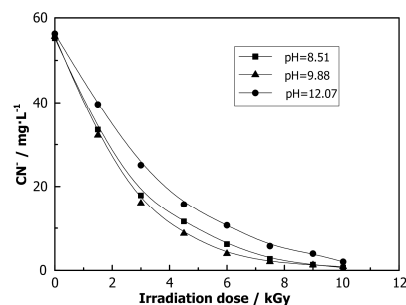


**Fig.11** Dependency of initial pH on electron beam radiolysis of cyanide solution.



**Fig.12** A comprison of O₃, EB, EB+O₃ on the decomposition of CN⁻ at different initial concentrations.

$$\cdot H + O_3 \rightarrow HO_3\cdot,\ k{=}3.6{\times}10^{10}\,dm^3mol^{-1}s^{-1} \quad (14)$$

$$HO_3\cdot \leftrightarrow O_3\cdot^- + H^+,\ pK{=}\,6.1 \quad (15)$$

$$e_{aq}^- + O_3 \rightarrow O_3\cdot^-,\ k{=}3.7{\times}10^{10}\,dm^3mol^{-1}s^{-1} \quad (16)$$

$$O_3\cdot^- + H^+ \rightarrow \cdot OH + O_2,\ k{=}9.0{\times}10^{10}\,dm^3mol^{-1}s^{-1} \quad (17)$$

$$\cdot OH + O_3 \rightarrow HO_2\cdot + O_2,\ k{=}1.1{\times}10^8\,dm^3mol^{-1}s^{-1} \quad (18)$$
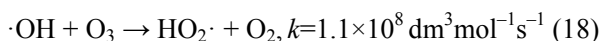
For $O_3$ alone, $CN^-$ removal efficiency was 27.14%, 22.77% and 18.22%, respectively. For EB alone, $CN^-$ removal efficiency was 59.25%, 42.17% and 33.88%, respectively. But the removals of $CN^-$ significantly increased up to 82.62%, 59.92% and 48.19%, respectively, in the case of EB+$O_3$. It is obvious that the extent of cyanide degradation by EB+$O_3$ approximately corresponded to the sum of the decay with EB and with $O_3$. Smilar results are reported in the literature for catechol[40]. To achieve the same effect by EB alone, the irradiation dose required will be increased from 1.5 kGy to 3 kGy. That is to say, the processing ability of EB-irradiation is increased by 1 times with 2 mg/L $O_3$ concentration.

**Continuous stability experiment:** Stability experiment were carried out a week with a water regulating tank, in which influent $CN^-$ concentration was controled at (15±2) mg/L, pH 9–9.5. The irradiation dose was 12 kGy during the irradiation process. From Fig.13, it can be seen that the outlet $CN^-$ concentration were under 0.5 mg/L after EB irradiation, which had met the discharge standards. Considering previous study made by Wang *et al.*[41], who had investigated the factors that influenced the efficiency of radiation-induced degradation of sodium cyanide by high energy electron beam. We may safely draw the conclution that it is feasible to remove cyanide from wastewater by EB irradiation.
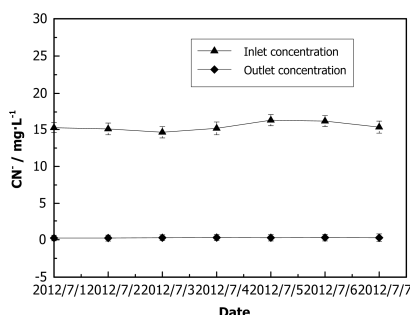


**Fig.13** Effect of EB irradiation on $CN^-$ concentration followed over 7 days.

## 4　Conclusion

Using the results obtained by bench-scale and pilot plant experiments, followed conclusions are outlined:

Cyanide was removed rapidly at a lower initial concentration than that a higher initial concentration under both γ- and EB-irradiation. In addition, the radiation induced decomposition of cyanide was observed as pseudo-first-order kinetic over the applied initial concentrations.

The characteristics of water solution, such as water composition and pH, have significant effects on the decomposition of cyanide. These observations supported the decomposition of cyanide was greatly initiated by ·OH radicals while direct $e_{aq}^-$ attack to cyanide plays a minor role.

The results show that removal efficiency of cyanide was higher in aerated than in de-aerated and static systems. Ozone can increase the effectiveness of ionizing irradiation. The processing ability of EB-irradiation was increased by 1 times with 2 mg/L $O_3$ concentration.

It is feasible to treat waste gas containing cyanide combined chemical absorbtion and radiaiton degradation according to the stability experiment. During the process of absorption and irradiation, cyanate and ammonia were found to be the main nitrogen-containing byproducts of cyanide.

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